

Computational Modeling of Uranium Hydriding and Complexes

K. Balasubramanian, W.J. Siekhaus, W. McLean II

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Computational Modeling of Uranium Hydriding and complexes

K. Balasubramanian, Wigbert J. Siekhaus and William McLean II
Chemistry and Material Science Directorate, Lawrence Livermore National
Laboratory, University of California, Livermore CA 94550

1. Introduction

Uranium hydriding is one of the most important processes that has received considerable attention over many years¹⁻⁷. Although many experimental and modeling studies have been carried out concerning thermochemistry, diffusion kinetics and mechanisms of U-hydriding, very little is known about the electronic structure and electronic features that govern the U-hydriding process. Yet it is the electronic feature that controls the activation barrier and thus the rate of hydriding. Moreover the role of impurities and the role of the product UH_3 on hydriding rating are not fully understood.

An early study by Condon and Larson¹ concerns with the kinetics of U-hydrogen system and a mathematical model for the U-hydriding process. They proposed that diffusion in the reactant phase by hydrogen before nucleation to form hydride phase and that the reaction is first order for hydriding and zero order for dehydriding. Condon² has also calculated and measures the reaction rates of U-hydriding and proposed a diffusion model for the U-hydriding. This model was found to be in excellent agreement with the experimental reaction rates. From the slopes of the Arrhenius plot the activation energy was calculated as 6.35 kcal/mole. In a subsequent study Kirkpatrick³ formulated a close-form for approximate solution to Condon's equation. Bloch and Mintz⁴ have proposed the kinetics and mechanism for the U-H reaction over a wide range of pressures and temperatures. They have discussed their results through two models, one, which considers hydrogen diffusion through a protective UH_3 product layer, and the second where hydride growth occurs at the hydride-metal interface. These authors obtained two-dimensional fits of experimental data to the pressure-temperature reactions. Kirkpatrick and Condon⁵ have obtained a linear solution to hydriding of uranium. These authors showed that the calculated reaction rates compared quite well with the experimental data at a hydrogen pressure of 1 atm.

Powell et al.⁶ have studied U-hydriding in ultrahigh vacuum and obtained the linear rate data over a wide range of temperatures and pressures. They found reversible hydrogen sorption on the UH_3 reaction product from kinetic effects at 21 °C. This demonstrates restarting of the hydriding process in the presence of UH_3 reaction product.

DeMint and Leckey⁷ have shown that Si impurities dramatically accelerate the U-hydriding rates.

We report our recent results of relativistic computations⁸ that vary from complete active space multi-configuration interaction (CAS-MCSCF) followed by multi-reference configuration interaction (MRSDCI) computations that included up to 50 million configurations for modeling of uranium-hydriding with cluster models will be presented.

2. Results

Figure 1 shows our computed potential energy surface for the insertion of a U site into H₂. As seen from Fig.1, pure U site has to surpass a barrier of 20.9 kcal/mole for the U-hydriding. Once the barrier is surpassed a stable product is formed which is 22.4 kcal/mole more stable than the reactants. Figure 2 shows the potential energy surface of an additional H₂ approaching UH₃ as modeled by U⁺³ interaction with H₂. The product UH₃ is highly ionic and thus U transfers electron density to the three hydrogens resulting in a U⁺³ state. As seen from Fig.2, U⁺³ inserts into H₂ spontaneously thus demonstrating the U³ -site in the product UH₃ binds to H₂ spontaneously forming a complex in which H₂ is separated far enough so as to cause liberation of H atoms in the presence of U.

3. Discussion

Our computed potential energy surfaces demonstrate a 21 kcal/mole activation energy barrier for pure U reaction with H₂. However, the presence of the product UH₃ catalyzes the U-hydriding. We have also modeled the presence of Si impurities for the U-hydriding reaction to show that the activation barrier is lowered by the presence of Si. Our computations reveal an electron donor-acceptor model for the U-hydriding, where H₂ exchanges electronic density from its occupied 1 σ_g orbital to the U(6d σ) orbital and back donation from the U(6d π) orbital back to H₂ 1 σ_u antibonding orbital causes the dissociation of H₂ by U. In particular the 5f or 7s orbitals of U are not involved in the dissociation of H₂. We also show that Si impurities assist the hydriding process by the spontaneous insertion of the ¹D state of Si into H₂. The UH₃ product catalyzes the hydriding process by spontaneous formation of a complex of H₂ at the U⁺³ site, which opens up the H₂ bond sufficiently to cause further U-hydriding to occur spontaneously. The bond breaking process in the formation complex assists the formation of H atoms in

the presence of U. The hydrogen atoms thus formed diffuse through the cracks to cause further U-hydriding thus explaining the experimental observation of Powell et al.

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We have calculated a 21 Kcal/mole activation barrier for the U-hydriding

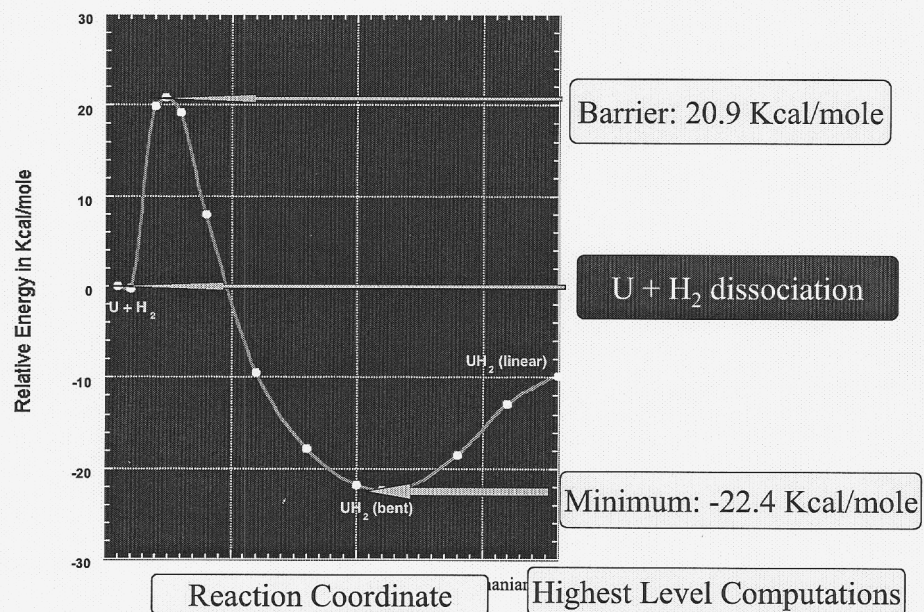


Figure 1 Potential Energy Surface for U-H₂ reaction

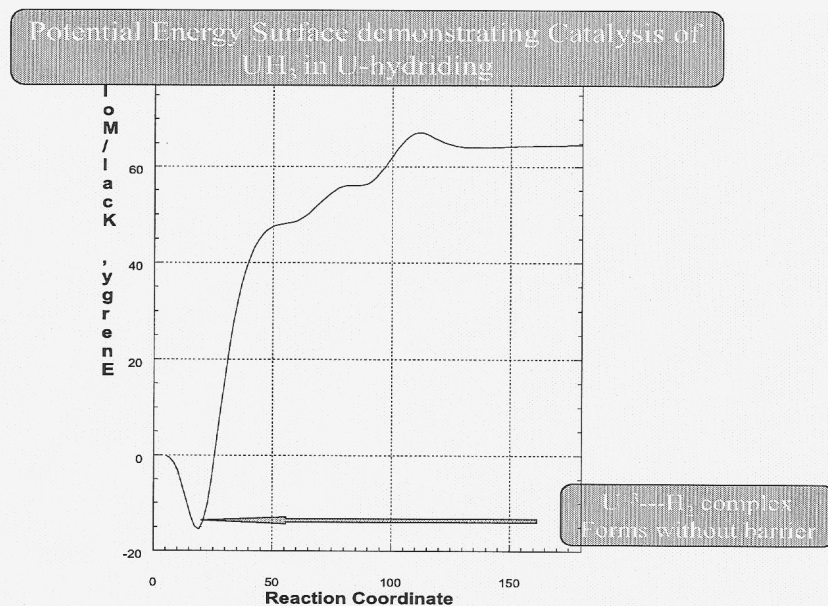


Figure 2 Potential Energy Surface for UH₃-H₂ interaction